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**Carderock Division
Naval Surface Warfare Center**

Bethesda, Md. 20084-5000

CARDIVNSWC-SSM-64-94/12 July 1994

Survivability, Structures, and Materials Directorate
Technical Report

AD-A284 058



Thermoelectric Properties of Conducting Polymers

by
Barbara Howell, Ph.D.

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ABSTRACT

Development of an inexpensive thermoelectric material which has a better cooling capacity than any currently available would have many practical advantages. On board ships or submarines it would allow a quiet, decentralized cooling architecture, it would reduce usage of chlorofluorocarbons, and would provide less expensive and lighter weight cooling systems. To this end a number of organic materials have been obtained and tested for thermoelectric properties. These include conductive vinyl elastomer, conductive nylon 12, and conductive polyphenylene sulfide, all of which are made conductive by addition of carbon. Polymers made conductive in this way do not have a high Seebeck coefficient. Other polymers tested include polyaniline, a Schiff's base polymer [poly-N,N'(1,3-phenylenedimethyldiylidene)bis(3-ethynylaniline)], TTF-TCNQ (tetrathiafulvalinium tetracyanoquinodimethanide), $D_8(\text{TCNQ})_2$ [1,2-bis(4-N-methylpyridylium-TCNQ)ethane], and polyoctylthiophene (POT) doped (separately) with 33% of the following substances: iodine, tetraethylamineammonium tetrafluoroborate, potassium persulfate, and ferric chloride. Ferric chloride doped POT was found to have a high Seebeck coefficient (1800 $\mu\text{V}/^\circ\text{C}$), but the conductivity (0.0074 S/cm) is not high enough to provide a good figure of merit.

KEYWORDS: Polyaniline, conducting polymer, conductive vinyl, conductive nylon, conductive polyphenylene sulfide, polyoctylthiophene, Schiff's base, thermoelectric.

ADMINISTRATIVE INFORMATION

The work described in this report has been supported by the In-House Laboratory Independent Research Office of the Naval Surface Warfare Center (Carderock Division) under Program Element 61152N, Project No. 1-8210-155.

INTRODUCTION

A thermoelectric material is one which becomes cooler when it carries an electric current. Thermoelectric cooling devices are currently employed for small scale cooling devices such as laboratory cooling plates, small refrigerated chests and for clothing which cools. More efficient materials with this property could be used to replace vapor compression type air conditioners. Such devices would be especially useful to the Navy which uses more than 2000 vapor compression units on board ships at the present time. Thermoelectric cooling devices are small, quiet, and do not require large amounts of electric current, they can be configured to fit a decentralized ship architecture, and do not release environmentally harmful chlorofluorocarbons into the atmosphere. Development of large-scale thermoelectric devices would have important commercial applications as well.

The most successful thermoelectrics to date have been made from ceramic materials such as bismuth telluride. However, only small increases in the figure of merit for this material have been achieved in the last twenty years. The usefulness of a material as a thermoelectric is made by evaluation of the figure of merit,

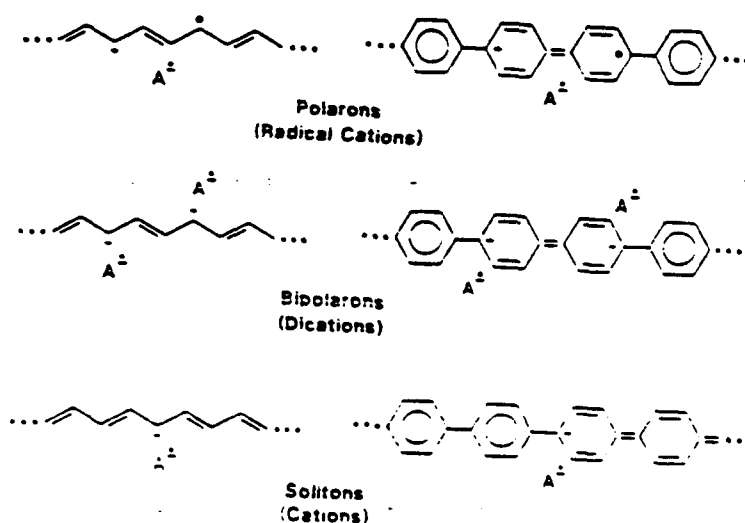
$$F = \frac{S^2 \sigma}{\kappa} \quad (1)$$

for which S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. The basic problem stems from the fact that increases in thermoelectric

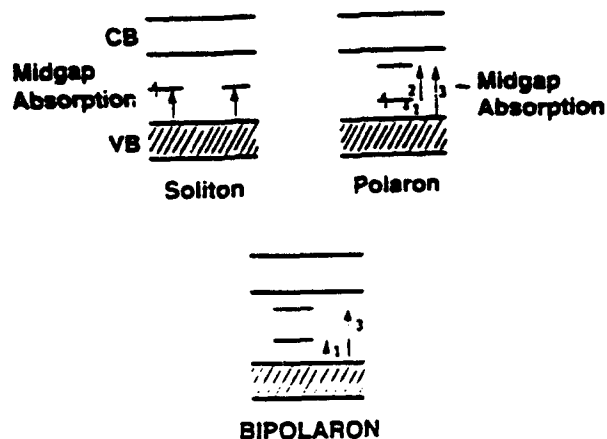
power can be achieved only by reduction of electrical conductivity and vice versa, whereas large values of both are needed for a good figure of merit. Furthermore, for ceramics, increases in electrical conductivity are accompanied by increases in the electronic contribution to thermal conductivity, and may not increase the figure of merit as may be seen from equation (1).

Conducting polymers are of interest because they have small values for the thermal conductivity [approx 10^{-3} W/(cm-K)], as compared with metals or ceramics, and this improves the figure of merit. In addition they have a low density, the electrical conductivity can be as large as 10^4 - 10^5 S/cm, and some have fairly large Seebeck coefficients. Therefore, an attempt to produce polymers with large figures of merit is worthwhile.

In addition to conduction by electrons, current is carried by unusual species in conducting polymers; these are solitons, polarons, and bipolarons for which examples are shown below.



In addition to carrying a positive charge, polarons also have an unpaired electron. When these carriers are generated, energy levels which lie within the bandgap region between the conducting and the valence bands, are created as shown.



When the band gap region is nearly filled with electrons, the charge carrier is positive, but when the band is nearly empty, charge is carried by negative species (Wang, 1993). Seebeck coefficient is largest when the band is nearly full or nearly empty, but the conductivity is largest in the intermediate region. Since a large figure of merit requires both a high conductivity and a large Seebeck coefficient, it is difficult to develop a material with high thermoelectric performance. Manipulation of absorption energy can be achieved by changing the oxidation state of the conducting polymer, changing the doping level, or by creation of anisotropy, e.g., by stretching a thin polymer film. The relationship among various factors affecting the Seebeck coefficient are shown in Fig. 1. In addition to conductivity, number of carriers and heat transmission is

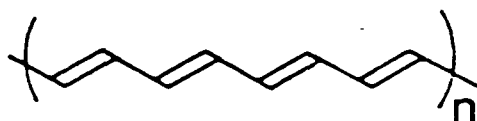
important. The electrons responsible for electrical conductivity in metals also allow heat transmission by electrons, K_e in Fig.

1. Heat transmission in polymers is by means of lattice vibrations, K_l which do not contribute to electrical conductivity.

Previous work with conducting polymers includes measurement of Seebeck coefficients for: polyacetylene, polyaniline, polythiophene, polyparaphenylene, poly(p-phenylenevinylene), and polypyrrole. For these substances, the emphasis has been on measurement of Seebeck coefficient as a means of probing polymer structure rather than being directed toward achieving large values for thermoelectric efficiency.

Polyacetylene

Polyacetylene was the first polymeric material to be made conductive. Its discovery generated enormous interest on the part of the scientific community and a major part of the theoretical effort made to describe electrical properties in conducting polymers has been devoted to this substance. It has the following structure



Measurements on polyacetylene doped with transition metal halides were made by Park et al (1989). Dopants were FeCl_3 (6%, $S=18.4$), MoCl_5 (5.2%, $S=13.5$), NbCl_5 (7.0%, $S=17.3$), ZrCl_4 (1.2%,

$S=28.7$), WCl_6 (1.1%, $S=46.2$), and $TaCl_5$ (1.0%, $S=84.9$). The units of S are microvolts/K and all thermopowers are positive. Even though $TaCl_5$ has a fairly high thermopower, its conductivity is low (0.06 S/cm) and therefore the figure of merit is also low. For this sample the temperature dependence is best described by the variable range hopping mechanism. For stretched samples, doped with $FeCl_3$, the conductivity was as high as 30,000 S/cm at 220 K when measurements were made on films 5mm x 1mm x 0.01mm. A structure consisting of highly conducting regions separated by resistance barriers is consistent with the temperature dependence of the thermopower data for the samples with high conductivity.

For material prepared by Yoon et al (1991), electrical conductivity parallel to the stretching direction in a polyacetylene film was found to be 6400 S/cm and the ratio of conductivity parallel to conductivity perpendicular was 25 S/cm and temperature independent. For the heavily doped polymer, thermopower was found to be linearly dependent upon temperature; however, the intercept for 0 K was found to change from positive to negative as amount of doping was increased. Behavior was similar for doping with $NbCl_5$, but for doping with $FeCl_3$ and $ZrCl_4$, the change in sign was not observed. In this work, doping with $MoCl_5$ at several different levels was done in order to investigate the mechanism of the transition from semiconducting to metallic behavior which occurred as the doping level was increased. The data obtained by these investigators fit the relation

$$S(T) = AT + BT/(T + T^0) \quad (2).$$

Behavior changes from semiconducting to metallic when the doping level reaches 1% of the number of CH=CH units ($y=1\%$), and the density of states becomes saturated when y is greater than 5%.

Zuzok et al (1991) measured thermoelectric power of polyacetylene doped with iodine. Freshly prepared samples containing 0.8% iodine showed a thermoelectric coefficient of 120 microvolts/K which was nearly independent of temperature. For unstretched samples containing 22% iodine, the conductivity was 3000 S/cm, and for stretched samples the conductivity rose to 5000-6000 S/cm. Figures of merit were not reported by these investigators. Thermopower for most samples decreased to zero at absolute zero, and the increase of S with temperature was sublinear, becoming nearly linear at the highest doping levels. For 9% iodine doping, S dependence upon temperature followed a $T^{1/2}$ dependence which would be expected if variable range hopping is the conductivity controlling mechanism. For the most highly doped samples with 22 and 28% iodine, conduction is metallic in nature with extremely small electron phonon interactions. For all samples studied by these investigators, S and the electrical conductivity were found to be inversely related.

An extremely high Seebeck coefficient, 11,600 $\mu\text{V/K}$, with a conductivity of around 1 S/cm, was found for cis-polyacetylene doped with iodine (1.6×10^{-4} mol/L) by Chien et al (1985). These values yield a figure of merit equal to 0.132, if the thermal conductivity is assumed to be 10^{-3} , a figure much higher

than that for bismuth telluride which has a FOM of about 10^{-8} ; however, the instability of polyacetylene in air precludes its use in a practical cooling device.

Dependence of Seebeck coefficient on temperature and electrical conductivity has been given by Pukacki et al (1991) to be

$$S = \frac{\pi^2 k}{3 e} kT \left[\frac{d(\ln \sigma(E))}{dE} \right]_{E_F} \quad (3)$$

for which $\sigma(E)$ is the electrical conductivity, E is the electron energy, and the other symbols have their usual significance. The electron energy is the product of the mobility of charge carriers, μ , their density, n , and the electron charge. However, if it is found that the mobility is independent of electron energy, for positive charge carriers, a different relation is applicable

$$S = \frac{\pi^2 k}{3 |e|} kT \eta(E_F) \quad (4)$$

for which $\eta(E)$ is the density of states per charge carrier. For non-segmented polyacetylene with 0.26 iodine atoms per CH unit, $S = (k/|e|)(7.8 \times 10^{-4})T$ and $\eta(E_F) = 0.25$ states per eV per carbon atom. These values are found to agree with the density of state values obtained when the variable range hopping model is applied to segmented samples. For very low doping levels, thermopower was found by these investigators to be large and independent of temperature. In this situation, there is a small concentration of carriers hopping among localized states.

When kinetic energy is found to be negligible, for a

bandwidth less than kT , and for carriers with a spin of $-1/2$, thermopower is given by the relation

$$S = \frac{k}{e} \ln \frac{2-\rho}{\rho} \quad (5)$$

for which ρ is the number of carriers per site. For this situation S increases as the doping level decreases, and its value is enhanced by structural disorder due to defects. For polyacetylene which is moderately doped and is segmented, S dependence on temperature has been found to follow the relation

$$S = AT + BT^{0.5} \quad (6).$$

Unlike metallic materials, which conduct heat principally by means of electrons, polymers conduct heat by means of phonons (lattice vibrations). For an isotropic medium, the phonon thermal conductivity has been given by Piraux et al (1991) by the relation

$$K_g = 1/3 cvl \quad (7)$$

for which K_g is the phonon thermal conductivity, c is the specific heat at constant volume, v is the velocity of sound in the medium, and l is the phonon mean free path. Phonon mean free path is related to τ , the phonon relaxation time by the relation

$$l = v\tau \quad (8)$$

However, a contribution to heat conduction may also be made by the charge carriers in a conducting polymer. Their contribution may be expressed by

$$\kappa = L_0 T \sigma \quad (9)$$

for which L_0 is the free electron Lorenz number and equals

$$L_0 = 2.45 \times 10^{-8} \text{ v}^2/\kappa^2 \quad (10).$$

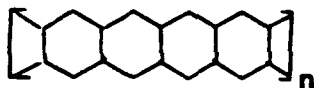
In these expressions σ is the electrical conductivity and T is the absolute temperature.

Polyacetylene also carries charge by positively charged carriers (solitons) which exist in only a few materials, such as polyacetylene and polyphenylene.

Although a great deal of theoretical and experimental work has been done with polyacetylene, its usefulness is severely limited by its instability in air.

Polyacenes

Polyacenes have been investigated by Ueno (1989) et al. They are characterized by having fused rings, e.g.,



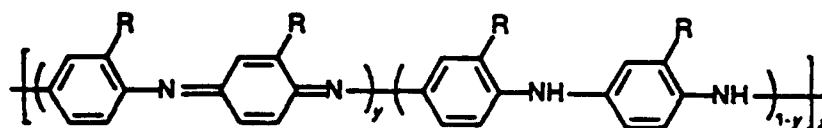
For sodium and lithium doped polymer, pyrolyzed to higher than 935 °C, metallic conductive fragments which exhibited both p-type and n-type behavior were observed. For samples heat treated at 650 °C, the Seebeck coefficient was -125 $\mu\text{V/K}$ with a conductivity of 10^{-9} S/cm for which the negative sign of S indicates that electrons are the charge carrying species. Since conductivity temperature dependence of n-type material cannot be explained by n-type nearly filled band theory, it was concluded that both both n-type and p-type carriers are involved in conductivity for the samples heat treated at the lower

temperature also.

Polyaniline

Unlike polyacetylene, conductivity in polyaniline occurs by means of polarons (radical cations) and bipolarons (dications).

Polyaniline has the following structure



As is the case for most conducting polymers, polyaniline has regions with high electrical conductivity but these are separated by insulating regions. The existence of small metal-like particles in the polymer with localization of polarons and bipolarons at chain ends can be used to account for the temperature dependence of their Curie spins (Ginder 1989), spins which are localized or poorly delocalized. For the protonated emeraldine form of polyaniline (polyaniline with equal numbers of reduced and oxidized repeat units), S is $-10 \mu\text{V/K}$ and has a conductivity of 0.5 S/cm .

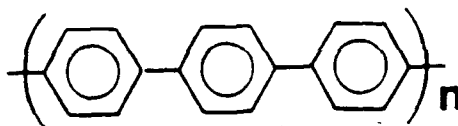
Polyaniline can be made conductive, when it is deposited from a solution onto an electrode, by the presence of hydrogen ions in the deposited film. Kuczkowski (1988) has reported a Seebeck coefficient of $+30 \mu\text{V/K}$ for polyaniline equilibrated to pH 9.6 when it is electrodeposited.

Polyaniline doped with camphor sulfonic acid (PANI-CSA) and blends of polyaniline with poly(methyl methacrylate) (PMMA) also doped with camphor sulfonic acid were studied by Yoon et. al

(1993). The value found for S was $10 \mu\text{V/K}$ at room temperature, and the conductivity was 280 S/cm . Thermoelectric power was found to increase linearly in proportion to temperature even when PANI was diluted with PMMA to volume fractions of PANI-CSA of 1%. Results are interpreted to mean that charge transport occurs at metal-insulator boundaries and along interconnected pathways of PANI-CSA with hopping transport between conducting regions. Hopping transport occurs because of the existence of unoccupied localized electronic states near the Fermi level. (At absolute zero, the Fermi level is defined as that energy for which all lower energy states are filled with electrons and all higher ones are empty. At higher temperatures there are some electrons above this level and some unoccupied electronic sites below this level (holes)). It is concluded that PANI-CSA is a Fermi glass, a material in which energy states are localized, but its structure is close to the metal-insulator transition boundary, beyond which the states become delocalized.

Polyparaphenylene and Polyparaphenylene vinylene

Ueno et al (1986) investigated the behavior of heat-treated polyparaphenylene (PPP) films which had been heated to 2800°C in an argon atmosphere. Polyparaphenylene has the following structure



Electrochemically grown (PPP) films were undoped electrochemically and found to be stable in air at room temperature. Heating at 600 °C to 1000 °C caused large increases in the electrical conductivity which were attributed to carbonization since the ratio of hydrogen to carbon decreased rapidly above 600 °C. At 800 °C metallic conductivity was observed in small carbonized fragments. Conductivity values as high as 400 to 510 S/cm were found at 2800 °C. Conductivity increases were accompanied by an increase in hole density and increased conduction by positive charge carriers.

Changes in thermopower were also measured. At 600 °C the thermopower was positive and had a value of around 12 $\mu\text{V/K}$. The value decreased to around 3 $\mu\text{V/K}$ at 1000 °K and then increased again reaching 10 $\mu\text{V/K}$ at 2800 °C. At heat treatment temperatures of 2500 °C, there was reported to be a decrease in the number of holes (carriers), an increase in the number of crystallites, and an increase in the carrier mobility. The data fit the model for three-dimensional variable range hopping, and behavior was similar to the behavior of nongraphitizable carbon since a three dimensional graphite was not developing. Dependence of thermopower on temperature was observed to fit the relation

$$S(T) = AT + BT^{1/2} \quad (11).$$

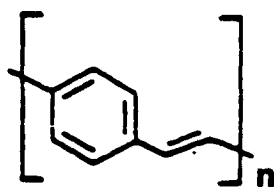
Equation (2) was also followed. A in equation (11) can be expressed as

$$A = \frac{\pi^2}{3} \frac{k_B^2}{|e|} \eta(E_F). \quad (12).$$

As reported for other conducting polymers, there is metallic conduction within the metal-like graphite particles with hopping occurring through the insulating regions.

Manipulation of the electrical properties of polyparaphenylene has been described by Bredas (1994). The bandgap can be manipulated by introduction of dimethoxyphenylene groups into the polymer chain which reduces the value of E_g from 2.5 eV to 2.1 eV. PANI groups may also be used for this purpose. Deposition onto an aluminum electrode can serve as a means of introducing electrons into the polymeric structure and thereby reducing the bandgap. When this is done, aluminum can form a covalent bond with carbon atoms of the vinylene group in the polymer backbone of the polyparaphenylene providing a more electron rich structure which is a better electrical conductor. Sodium and calcium do not form covalent bonds with the polymer, but they can be used to modify the bandgap by functioning as dopants. In related work Bredas et al (1984) have shown, by means of STO-3G calculations, that in paraphenylene, sodium bonds to the phenylene ring with nearly complete charge transfer (0.93e) to the ring reducing the band gap from 0.1568 to 0.0975 eV.

In marked contrast to polyparaphenylene, polyparaphenylene vinylene (PPV) films were found to be highly graphitizable and were studied by Ueno and Yoshino (1986a and b) to heat treatment temperatures of 2900 °C. PPV has the following structure



PPV

The conductivity is found to increase rapidly at 600 °C because of increases in carrier density and carbonization which occurs with decreases in the H/C ratio. Between 1000 °C and 2000 °C, crystalline growth occurs and there is a decrease in carrier density. For stretched film and a heat treatment temperature of 3000 °C, the electrical conductivity reaches 1.6×10^4 S/cm, a value comparable to the conductivity of highly ordered pyrolytic graphite and benzene-derived graphite fiber. For a heat treatment temperature (HTT) of 2900 °C, the unstretched film has a conductivity of 8100 S/cm. Above 2000 °C there is development of a three-dimensional graphitic structure which is well developed at 2900 °C. Three dimensional variable range hopping was found to give way to metallic conductivity as the polymer was converted to well graphitized carbon.

Thermopower changes as the graphitic content changes. At 600 °C the thermopower is around 7 μ V/K, it decreases at 1000 °C to 3 μ V/K but increases once again as the number of holes decreases and there is an increase in crystallinity to a maximum of 7 μ V/K at 2000 °C, then decreases and reaches -5 μ V/K after heat treatment at 2900 °C. The switch to a negative value indicates a change from conduction by holes to conduction by

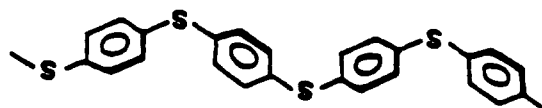
electrons. Equation (2) was used to calculate the density of states per carrier at the Fermi level. These were found to be

$\eta(E_f)$ (States per carrier)	1.88	0.82	1.50
HTT ($^{\circ}\text{C}$)	800	1000	2000
S ($\mu\text{V/K}$)	7	3	7

It is interesting to note that for the stretched film with a heat treatment temperature of 1000 $^{\circ}\text{C}$, the thermopower perpendicular to the stretch direction is much larger than that parallel to the stretch direction, and that this film has conducting carbonized metallic fragments which are well ordered along the stretch axis. Electrical conductivity is limited by the carrier hopping which must occur between the carbonized fragments. The conductivity differences in the perpendicular and parallel directions are caused by differences in the carrier mobilities in the two directions.

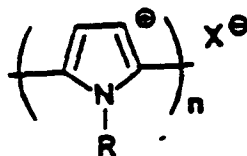
Polyphenylene sulfide (Ryton)

A conductive form of this material, which is commercially available, is made conductive by the presence of carbon and has the following structure:



Polypyrrole

Polypyrrole is a much more stable chemical species than polyacetylene and would be a reasonable candidate for a thermoelectric device if it could be doped to give it a high Seebeck coefficient. It has the following structure:



Measurement of S on electrochemically prepared and dedoped polypyrrole has been made by Maddison et al (1988) who state that in general, thermopower in conducting polymers tends to have a temperature dependence which lies between $T^{0.5}$ and $T^{1.0}$. This implies that there is a metal-like component as well as variable range hopping contributing to thermopower. Thermopower measurements for polypyrrole are reported for the temperature range 4 to 350 K by these investigators. At the higher temperatures in this range, variable range hopping temperature dependence of conductivity is observed, and the Seebeck coefficient is found to be linearly dependent on temperature. S is positive and has the value $5 \mu\text{V/K}$ at 200 K, increasing to $40 \mu\text{V/K}$ at room temperature. S values decrease as electrical conductivity increases as has been noted for other conducting polymers.

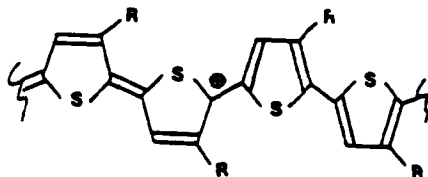
Thermopower of polypyrrole (PPy) doped with benzenesulfonate

and perchlorate ion was measured by Bender et al (1987). For the benzenesulfonate doped PPy at room temperature, the highest thermopower measured was $5 \mu\text{V/K}$ and for PPy doped with perchlorate, the value was found to be $10 \mu\text{V/K}$ for unaged samples. After 80 days the benzene sulfonate doped sample showed no change in its thermopower, but after 80 days this value for the perchlorate sample had decreased to half its former value. Aging studies were made at temperatures from 0 to 350 K.

Electrochemically prepared PPy, doped with BF_4^- , has been studied by Roy et al (1991). A p type thermopower of $34 \mu\text{V/K}$ was found for films $81.7 \mu\text{m}$ thick and the density of states was found to be $3.09 \times 10^{30} \text{ states eV}^{-1}\text{cm}^{-3}$.

Polythiophenes

Polythiophenes, which have the following structure,



have been studied by Elsenbaumer et al (1986). These investigators studied alkyl derivatives of 2,5-polythiophenes with iodine, nitrosyl salts and antimony hexafluoride. When excess iodine was added to poly(3-n-butylthiophene) in 5 mL of methylene chloride, a conductivity of $2.9 (\text{ohm-cm})^{-1}$ was observed. Use of antimony hexafluoride salts provided the

greatest stability.

Measurement of Seebeck coefficients of polythiophenes has been made by Isotalo et al (1989) for polyoctylthiophene copolymerized with polyethylenevinylacetate. A Seebeck coefficient of $475 \mu\text{V/K}$ was found for ferric chloride dopant, with a conductivity of 10^{-5} S/cm . Ion implantation with 25 keV F^+ ions gave a thermopower of $420 \mu\text{V/K}$ and a conductivity of $1.4 \times 10^{-5} \text{ S/cm}$.

Schiff's Bases

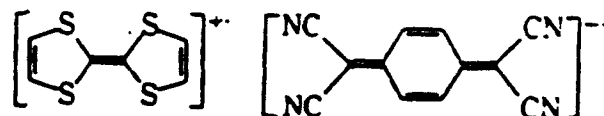
Schiff's bases are prepared by condensation of an aldehyde and an amine. The monomer



was prepared by Ted Walton (1987, 1989) who investigated its polymerization at elevated temperatures, and found that it was possible to produce a conductivity of approximately 100 S/cm by extensive heat treatment under argon to temperatures of 700° . It was further investigated by DiBerardino in this laboratory. The Seebeck coefficient, however, was not measured by these investigators.

TTF-TCNQ

Tetrathiofulvalinium-tetracyanoquinodimethanide (TTF-TCNQ) was the first organic compound shown to have electrical conductivity. It has the structure shown.



Its electronic properties were reviewed by Cohen et al (1976). Complexes of TCNQ with segments of several polymers were investigated by Rembaum, et al (1969) who reported a Seebeck coefficient of 1 mV/K for the TCNQ complex with 1,2-bis(4-pyridyl)ethane. However, the electrical resistivity is 4×10^6 ohm-cm, so that the figure of merit is low.

General considerations

Preparation of materials with greater thermoelectric power by production of quantum wells, made by splicing together thin layers of the material, has been theoretically predicted by Hicks and Dresselhaus (1992). Advantages of layering include reduced phonon thermal conductivity, since phonons are scattered between layers, along with increases in electrical conductivity within layers. Diffusion of materials from one layer into another, with consequent reduction in thermopower, may prove to be a fatal drawback in this type of material.

Electrical conductivity in iodine-doped polystyrene has been studied by Chakraborty et al (1991). Equations used by these investigators are relevant to the present work. Equations given include:

$$ST = (E_f - E_v) + 2kT \quad (13)$$

$$\rho = 2 \left[\frac{2\pi m^* kT}{h^2} \right]^{3/2} \exp \left[\frac{E_v - E_f}{kT} \right] \quad (14)$$

$$\text{and} \quad \sigma = \rho e \mu \quad (15)$$

In these expressions E_f is the energy of the Fermi level, E_v is the energy level of the top of the valence band, m^* can be taken as the mass of an electron, h is Planck's constant, σ is the electrical conductivity, ρ is the value found from equation (14), e is the electronic charge and μ is the carrier mobility.

EXPERIMENTAL¹

Materials

Polyaniline. A sample of emeraldine polyaniline (Versicon) was obtained from Allied Signal, Morristown, NJ 07962, and polyaniline was also obtained from Steve Hobaica (Code 641, NSWC) who prepared it by chemical means from the monomer.

Samples of vinyl elastomer, made conductive by addition of carbon, were obtained from Americhem, Cuyahoga Falls, Ohio 44221-3303. One (36009-C1) had a conductivity of 1.48 S/cm and the other (32523-C1) a conductivity of $1.62 \cdot 10^{-4}$ S/cm.

Conductive nylon 12 (30695-C1) with a bulk conductivity of 10^{-3} to 10^{-5} S/cm was also obtained from Americhem. Its

¹Occasionally, in order to describe procedures adequately, it has been necessary to identify equipment and sources of reagents. In no case does this imply Navy recommendation or endorsement.

conductivity was also due to addition of conductive carbon black.

Conductive polyphenylene sulfide (Ryton), containing a conductive filler, was obtained from Phillips 66 Co., Borger, TX 79008.

Poly-3-octylthiophene was obtained from NESTE Oy in Finland. Poly-3-octyl thiophene samples were separately combined with enough of the following materials to give 33%. Added materials were iodine, ferric chloride, tetraethylammonium tetrafluoroborate and potassium persulfate obtained from Aldrich Chem. Co. Solvents used for these mixtures were as follows: iodine, trichloroethylene; ferric chloride, toluene and ethanol; tetraethylammonium tetrafluoroborate, ethanol; and potassium persulfate, toluene and water. Solvents were removed with a rotary evaporator under vacuum at room temperature.

Schiff's base polymer was prepared from the monomeric N,N'-(1,3-phenylenedimethyldiyne)bis(3-ethynylaniline), Thermcon 2000, obtained from National Starch and Chemical Corp, Bridgewater, NJ 08807. Processing was done at CARDEROCKDIV, initially in air at 145 °C for one hour, 150 °C for two hours, 200 °C for one hour, at 250 °C for one hour, and at 300 °C for 50 hours. At this point the conductivity was too low to allow measurement of the Seebeck coefficient with the T.E. Technology device, so further heating was done under argon at 400, 500, 600, and 700 °C each for 100 hours in a high-temperature tube furnace. Flow rate of argon was maintained at 30 mL/min as measured with a Brooks Sho-Rate flowmeter. An exit tube of small diameter

insured that no oxygen back flow was possible.

TTF-TCNQ (tetrathiafulvalinium-tetracyanoquinodimethanide) was prepared by combining equimolar amounts of tetrathiofulvene with tetracyanoquinodimethane in acetonitrile solvent (Ferraris et al, 1973), from which the TTF-TCNQ precipitated.

$D_8(\text{TCNQ})_2$ (1,2-bis(4-N-methylpyridylium-TCNQ)ethane) was prepared from LiTCNQ and D_8I_2 as described by Rembaum et al (1969). LiTCNQ was prepared from LiI and TCNQ (Melby et al, 1962). D_8I_2 was prepared from methyl iodine and 1,2-bis(4-pyridyl)ethane (Rembaum et al, 1969) in toluene instead of benzene.

Reagents used to prepare TTF-TCNQ and $D_8(\text{TCNQ})_2$ were obtained from Aldrich Chem. Co., Milwaukee, WI 53233, and used without further purification.

Measurement

A device for measurement of figure of merit, Seebeck coefficient, and electrical conductivity was obtained from T. E. Technology, Inc., Traverse City, MI 49884. To utilize this device, the sample must have minimum dimensions of 0.79 x 0.79 cm on two sides and 0.32 cm on the remaining side, and have two parallel faces. It is also necessary to have excellent electrical contact with the thermocouples and the electrical leads of the measurement system. Thermoelectric properties of polymers with an electrical conductivity lower than 1 S/cm could not be measured with this device.

Leads to the T. E. Technology instrument were attached by use of a special solder which formed a good bond with polymer previously flame-spray coated with the metals bronze, zinc, or zinc followed by copper. The solder, Conducto-pen/PC board repair, contained tin (13%), lead (27%), bismuth (50%), and cadmium (10%) and melted at 70 °C. It can be purchased from Kapp Alloy & Wire, Inc., Oil City, PA 16301.

Powdered samples were pressed into pellets in an IR press at 10 tons, or else with a heated press.

Infrared spectra were run on a Beckmann IR 4260 research infrared spectrophotometer and UV/vis spectra were run on a Perkin Elmer 559 uv-vis spectrophotometer.

RESULTS AND DISCUSSION

Attachment of leads to the polymer samples to be measured in the T. E. Technology device, proved to be a major problem, and many means of attachment were tried. Conducting carbon and silver pastes, and a variety of conductive tapes failed to form bonds with high enough conductivity. Evaporation of gold onto the polymer surface was attempted with the sputter coater designed for preparation of samples for the scanning electron microscope. However, when soldering to this coating was attempted, the coating dissolved in the solder and no bond was formed.

An indium-gallium mixture did not work satisfactorily because it remained liquid after application, and posed a health

risk in addition.

However, flame spraying first with zinc and then with copper proved successful, since a sufficiently adherent coating was formed to allow leads to be soldered to the polymer with the low melting PC Board Repair solder.

Measurement of the thermoelectric properties of polyaniline was successfully done on pressed pellets with the T.E. Technology instrument in the Annapolis laboratory, but the figure of merit was found to be very low. It has been reported that polyaniline has a large Seebeck coefficient when its band gap is nearly filled or nearly empty, but in these cases its conductivity is low (Wang, 1993). Further work was not done with the polyaniline.

The polyphenylene sulfide carbon filled sample, which was obtained as a flat strip, and the pressed pellet nylon carbon filled sample had conductivities which were too low to permit measurement on the T. E. Technology device. Since, the carbon filled vinyl samples also lacked promising properties, further work was not done with the carbon filled samples. It was concluded that the electrical properties were contributed by the carbon, which conducts by movement of electrons and lacks the energy absorbing mechanism required to produce thermoelectric cooling.

Because of difficulty making measurements on the Annapolis device, polymer samples were sent to T. E. Technology in Traverse City, MI for measurement. For the device in use there,

electrical contact is made by pressure of the leads on the polymer surface, which avoids difficulties with attaching leads, and sample shape requirements are less stringent. Samples sent to Traverse City for measurement included TTF-TCNQ, $D_6(\text{TCNQ})_2$, Schiff's base, and the four poly-3-octylthiophene samples doped respectively with 33% ferric chloride, 33% potassium persulfate, 33% tetraethylammonium tetrafluoroborate, and 33% iodine.

Measurements obtained on these sample at T. E. Technology are shown in Table 1. Seebeck coefficients found for the various materials were low except for the FeCl_3 -POT which had the value $1800 \mu\text{V/K}$, a value much higher than that found for most other conducting polymers. If the heat conductivity is taken to be 10^{-3} , the figure of merit can be calculated with use of equation (1). It is 2.77×10^{-5} , which is two orders of magnitude lower than bismuth telluride. The electrical conductivity of this material (0.0074 S/cm) is too low to give a good figure of merit.

The Seebeck coefficient, $22 \mu\text{V/K}$, observed for the pyrolyzed Schiff's base is comparable to that seen for pyrolyzed PPP and PPV.

Equations (14), (15), and (16) are used to compare values for the ferric chloride doped POT, and for other substances for which conductivity and Seebeck coefficient data are available. Results are shown in Table 2. It is evident, when the exponential term in (15) is considered, that for a positive difference $E_f - E_v$, the number of carriers is smaller than if this difference is negative. Also the extreme variation in mobility calculated for

the different polymers indicates failure of the equations to predict charge carrier behavior. For the polyacetylene with $S = 11,600 \mu\text{V/K}$, the number of carriers calculated is close to zero, and for the POT-FeCl_3 , it is smaller than for the other substances in the table. When the number of carriers is smaller, the mobility calculated from (16) is much higher.

To improve the performance of POT-FeCl_3 , a larger electrical conductivity and hence more carriers are needed. From Fig. 1, it is seen that there is an optimal value for the product of conductivity and Seebeck coefficient and this value gives a value for optimal number of carriers, but what these values are for POT-FeCl_3 is not known. It would be desirable to perform additional experiments with this material to establish concentrations providing the best performance.

Use of equation (14) gives the value 0.485 eV for the difference $E_f - E_v$, which translated into wavenumbers has the value 3912 cm^{-1} . The actual maximum absorbance of the complex, shown in Fig. 2, is 3380 cm^{-1} in reasonable agreement with the predicted value.

CONCLUSIONS

Electrical conductivities and Seebeck coefficients were measured for a number of conducting organic materials. It was found that pyrolysis of the Schiff's base compound did not produce a large Seebeck coefficient. Furthermore, addition of carbon to a polymer to make it conductive also failed to increase

this coefficient. Measured Seebeck coefficients were very small for all other polymers tested, with the exception of the ferric chloride doped polyoctylthiophene. When compared with values calculated for $E_f - E_v$ for other conducting polymers this value (0.502 eV) was found to be larger than for most of them, the number of carriers was smaller, and the carrier mobility was found to be much larger. Methods for altering conducting polymeric properties were suggested by Bredas (1994).

ACKNOWLEDGEMENT

Invaluable assistance from Thomas Gracik, Fire Protection and Survival Branch NSWCCD, who solved many of the experimental problems of this investigation and prepared the ferric chloride POT mixture, is acknowledged with sincere gratitude.

REFERENCES

- Bender, K., E. Gogu, I. Hennig and D. Schweitzer, *Synthetic Metals* 18, 85-88 (1987).
- Bredas, Oral presentation at Polymeric Materials, Sciences and Engineering, American Chemical Society Meeting, San Diego, March, 1994.
- Chakraborty, N. B. Palit, S. K. Das, & S. Basu, *Indian J. of Pure & Appl. Phys.* 29, 478-481 (1991).
- Chien, J. C. W., J. M. Warakowski, F. E. Karasz & M. A. Schen, *Macromolecules* 18, 2380-2389, (1985).
- Cohen, M. J., L. B. Coleman, A. F. Garito, & A. J. Heeger, *Phys. Rev. B* 13(11) 5111-5116 (1976).
- Elsenbaumer, K. R. L., K. Y. Jen, & R. Oboodi, *Synthetic Metals* 15, 169-174 (1986).
- Ferraris, J., D. O. Cowan, V. Walatka, Jr., & J. H. Perlstein, *J. Am. Chem. Soc.* 95(3), 948-949 (1973).
- Ginder, J. M. A. F. Richter, A. G. MacDiarmid, & A. J. Epstein, *Solid State Communications* 63(2), 97-101 (1987).
- Goldschmid, H. J. & J. R. Hanscomb, *J. Phys. C: Solid State Phys.* 11, L657-L659 (1978).
- Hicks, L. D., & M. S. Dresselhaus, submitted to *Phys. Rev. B* 15, Dec. 3, 1992
- Isotalo, H., *Comment. Phys.-Math. (Finland)* No. 108, 1-27 (1990).
- Kuczkowski, A., *Progr. in Colloid & Polym. Sci* 78 126-128 (1988).
- Park, Y. W., C. O. Yoon, C. H. Lee, H. Shirakawa, Y. Suezaki, and K. Akagi, *Synthetic Metals* 28, D27-D34 (1989).
- Pukacki, W., R. Zuzok, & S. Roth, *Synthetic Metals* 45 405-411 (1991).
- Rembaum, A., A. M. Hermann, F. E. Stewart, & F. Gutmann, *J. Phys. Chem.* 73(3) 513-520 (1969).
- Roy, R., S. R. Sen, M. Digar & S. N. Bhattacharyya, *J. Phys: Condens. Matter* 3 7849-7856 (1991).
- Ueno, H., G. Ishii, K. Yoshino, K. Tanaka, T. Yanahe, and S. Yata, *Synth Metals* 18(1-3), 515-520 (1987).

- Ueno, H., & K. Yoshino, J. Phys. Soc. of Japan 55(12), 4382-4387 (1986).
- Ueno, H., & K. Yoshino, Phys. Rev. B 34(10) 7158-7163 (1986).
- Walton, T. R., J. Appl. Polym. Sci. 33 971 (1987), *ibid.*, 37 1921 (1989).
- Wang, J., Massachusetts Inst. of Tech., oral communication, 1993.
- Yoon, C. O., M. Reghu, C. Moses, and A. J. Heeger, Phys Rev. B (19) 14080 - 14084 (1993).
- Zuzok, R., A. B. Kaiser, W. Pukacki, and S. Roth, J. Chem. Phys. 95(2) 1270 - 1275 (1991).

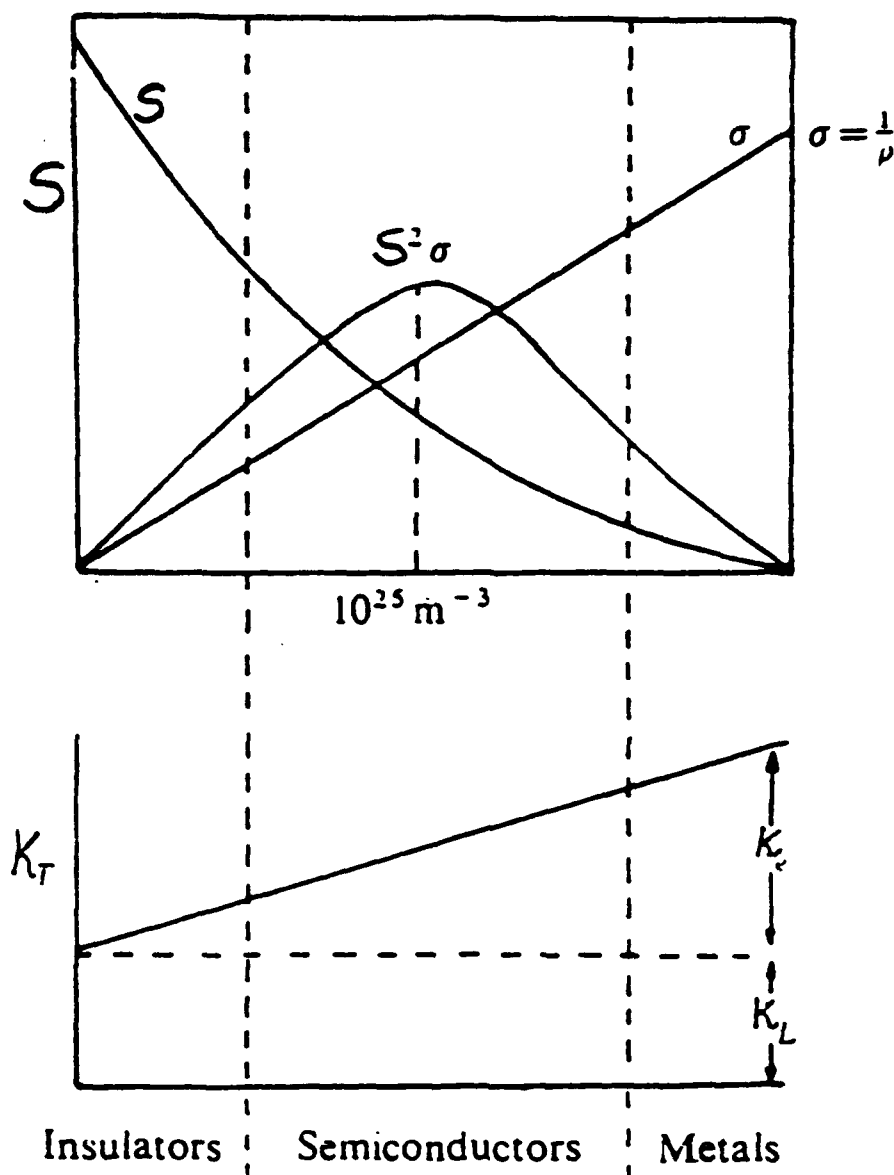


Fig. 1. Factors influencing choice of thermoelectric materials.

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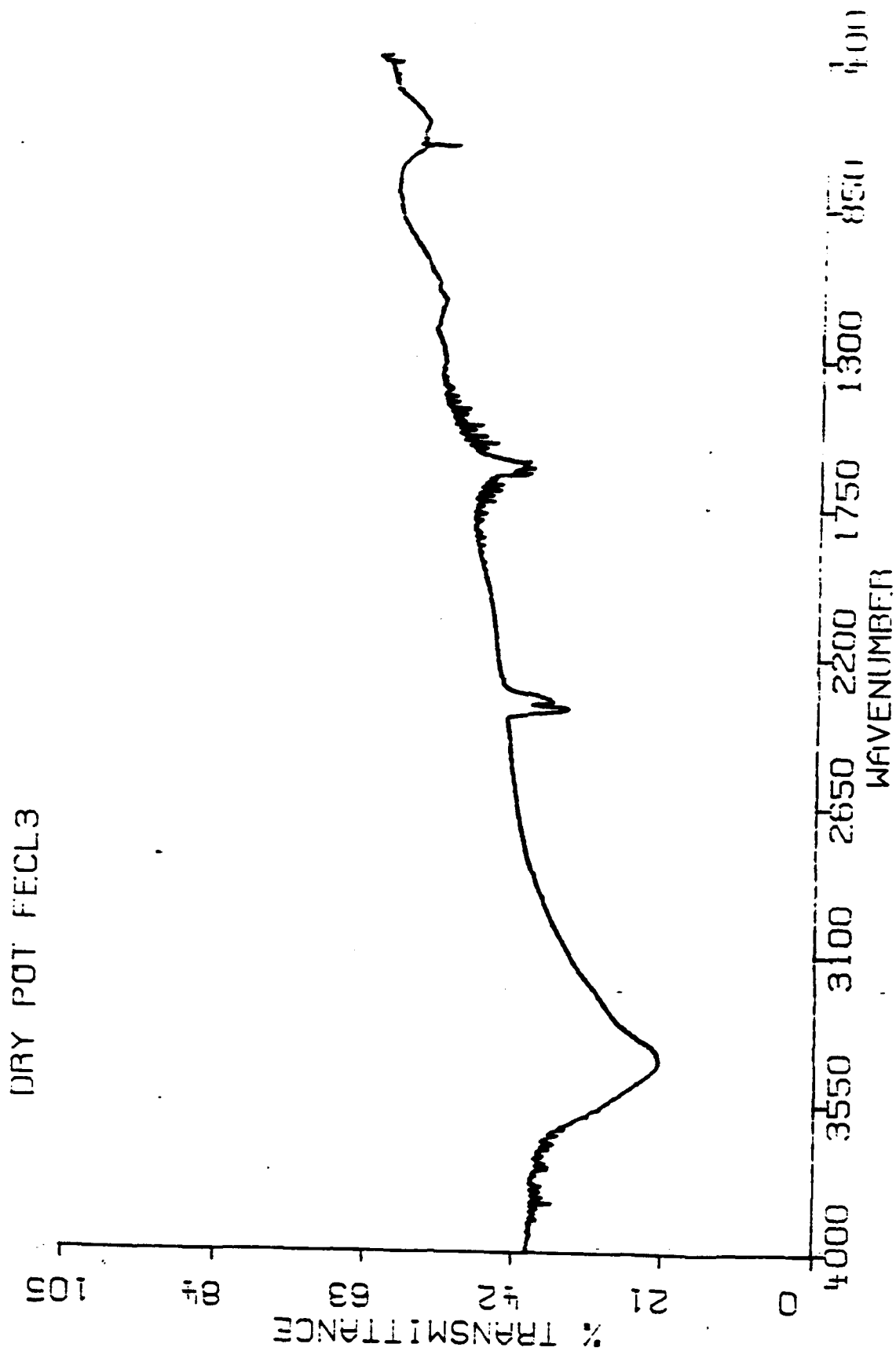


Fig. 2. Absorbance of POT-Ferric Chloride

TABLE 1.

Test Data on Polymeric Samples					
Test no.	Sample name	T (average) (°C)	DELTA-T (°C)	SEEBECK (μV/°C)	RESIST (ohms)
1.	POT FeCl ₃ Aug93-A	22.835	11.250	1824.11	38.5
2.	POT FeCl ₃ Aug93-A	22.853	11.215	1705.44	
3.	POT FeCl ₃ Aug93-A	22.863	11.645	1800.50	
4.	POT FeCl ₃ Aug93-B	22.713	9.125	*****	270000
5.	POT FeCl ₃ Aug93-B	22.765	9.070	*****	
6.	Schiff Base	22.943	11.675	22.43	7.1
7.	Schiff Base	22.933	11.665	22.56	
8.	Schiff Base 90 deg	23.015	13.590	21.22	
9.	POT persulfate Sep93	23.090	14.310	*****	184000
10.	POT persulfate Sep93	23.020	13.410	*****	
11.	POT TEATFB Sep93	23.160	14.240	*****	2000000
12.	DS(TCNQ)2 NSWC	22.958	13.125	-37.24	1017
13.	DS(TCNQ)2 NSWC	22.988	13.505	-37.17	
14.	TTF-TCNQ NSWC	23.158	14.375	3.74	3.3
15.	TTF-TCNQ NSWC	23.053	13.185	3.39	
16.	POT I2 Sep93-A	23.010	14.000	79.27	14.35
17.	POT I2 Sep93-A	22.988	13.015	79.62	
18.	POT I2 Sep93-B	23.024	13.750	78.33	9.8
19.	POT I2 Sep93-B	23.033	13.360	78.84	

Table 2. Properties of Conducting Polymers

Substance	Dopant	σ (S/cm)	S ($\mu\text{V/K}$)	E_g (eV)	$E_F - E_g$ (eV)	n (cc) ⁻¹	μ (cm ² /Vsec)
Polyoctylthiophene	FeCl ₃	0.0074	1800		0.485	1.16×10^{11}	4×10^5
Polyalkylthiophene ¹	Tetramethyl ammonium perchlorate	9.6×10^{-7}		1.42			
Polydialkylthiophene ²	Iodine	10	2.9	2.0-2.2	-0.05	1.74×10^{20}	0.359
POT-PVA ³	FeCl ₃	0.32	23	0.026	-0.0431	No. of spins less than 10^{17}	0.45
Polycetylene ⁴	Li	10^{-9}	-125 (650 °C HTT)		-0.068	$10^{17} - 10^{19}$ (775 °C HTT)	6.3×10^{-8}
Polycetylene ⁵	Iodine	1	11,600		3.43	0	
Polycetylene ⁶	TaCl ₅ (1%)	30,000	84.9		-0.025	6.5×10^{19}	2.9×10^3
Polyaniline ⁷	H ⁺ camphorsulfonic acid	0.5 300	-10 10		-0.054 -0.048	2.0×10^{20} 1.6×10^{20}	0.0153 11.6
Polyethylene-terephthalate ⁸ (Mylar)		3.1×10^{-6}	750	0.7	0.173	2.6×10^{16}	7.4×10^{-4}
Polypyrrole ⁹		9	40		-0.039	5.2×10^{18}	10.8
Polyparaphenylene ¹⁰		10^{-5}	12		-0.0479	3.8×10^{18}	1.64×10^{-5}
Polyphenylethynylene		10^{-5}	7		0.049	3.6×10^{18}	1.74×10^{-5}

1,2, Eisenberger et al. (1986). 3, Isotelo et al. (1989). 4, Ueno (1989). 5, Chiepp et al. (1985). 6, Park et al. (1989). 7, Yoon et al. (1993). 8, Goldschmid & Manscomb (1978). 9, Madisson et al. (1988). 10, Ueno et al. (1986).

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE July 1994		3. REPORT TYPE AND DATES COVERED RDT&E 9-91 to 6-94	
4. TITLE AND SUBTITLE Thermoelectric Properties of Conducting Polymers				5. FUNDING NUMBERS Program Element 61152N Task No. R004001 Work Unit 94-1-8210-155-20	
6. AUTHOR(S) Barbara Howell, Ph. D.					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Carderock Div. Naval Surface Warfare Center Annapolis Detachment, Codes 8210 & 6440 Annapolis, MD 21402-5067				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Technology ONT 224 Arlington, VA 22217-5000				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Development of an inexpensive thermoelectric material which has a better cooling capacity than any currently available would have many practical advantages. On board ships or submarines it would allow a quiet, decentralized cooling architecture, it would reduce usage of chlorofluorocarbons, and would provide less expensive and lighter weight cooling systems. To this end a number of organic materials have been obtained and tested for thermoelectric properties. These include conductive vinyl conductive nylon 12, and conductive polyphenylene sulfide, all of which are made conductive by addition of carbon. Polymers made conductive in this way do not have a high Seebeck coefficient. Other polymers tested include polyaniline, a Schiff's base polymer [poly-N,N'(1,3-phenylenedimethyldiylidene)bis(3-ethynylaniline)], TTF-TCNQ (tetrathiafulvalinium tetracyanoquinodimethanide), D ₈ (TCNQ), [1,2-bis(4-N-methylpyridylium-TCNQ)ethane], and polyoctylthiophene (POT) doped (separately) with 33% of the following substances: iodine, tetraethylamineammonium tetrafluoroborate, potassium persulfate, and ferric chloride. Ferric chloride doped POT was found to have a high Seebeck coefficient (1800 $\mu\text{V}/^\circ\text{C}$), but the conductivity (0.0074 S/cm) is not high enough to provide a good figure of merit.					
14. SUBJECT TERMS KEYWORDS: Polyaniline, conducting polymer, conductive vinyl, conductive nylon, conductive polyphenylene sulfide, polyoctylthiophene, Schiff's base, thermoelectric.				15. NUMBER OF PAGES 38	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited.		